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Controlling the electronic structure of nanocrystal assemblies by variation of the particle – particle interaction

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Abstract

The change in the electronic structure of germanium nanocrystals is investigated as their concentration is increased from non-interacting, individual particles to assembled arrays of particles. The electronic structure of the individual nanoclusters shows clear effects due to quantum confinement which are lost in the concentrated assemblies of bare particles. When the surface of the individual particles is passivated, they retain their quantum confinement properties also upon assembly. These effects are interpreted in terms of a particle – particle interaction model.

The vast majority of applications for nanocrystal material assemblies are based on solution-chemistry synthesized materials with a solid organic surface layer and relying on electric or longer-range interaction between well separated particles.¹ While particle size and morphology variability has been well documented and exploited,²⁻⁴ virtually nothing is known about the effects of immediate proximity on the actual electronic structure of nanocrystals. In this manuscript we will show how the intrinsic electronic properties of Ge nanoparticles change when we go from isolated non-interacting (initially bare) particles to a three dimensional assembly. For the investigation of particle – particle interaction effects on the electronic structure we start out with nanocrystals condensed out of the gas-phase.⁵ Only this route allows the synthesis of bare and contaminant free nanoparticles. The variation of particle – particle interaction is achieved by either varying the particle density and thus their distance, or by creating barriers in between them. In the following paper we first investigate the transition from sub monolayer depositions of isolated particles to multiple monolayers of touching particles. Then we study particle interaction effects as a function of particle surface termination with organic molecules. For this route a new in-situ particle passivation process has been developed.

The nanocrystals are condensed out of Ge vapor in a He buffer gas atmosphere and subsequently deposited on HF-etched silicon substrates.⁵ As cluster material germanium is chosen because it exhibits strong quantum confining properties.⁶ In Fig. 1 atomic force microscopy (AFM) images of germanium nanocrystal depositions on Si substrates are shown. For sub-monolayer depositions (left) randomly scattered, individual particles can be seen. When multiple layers of nanocrystals are deposited (right), particles on top of each other can be clearly distinguished. To investigate the electronic structure of the nanocrystals, X-ray absorption (XAS) experiments in total-electron-yield mode are conducted at the high resolution and high flux undulator beamline 8.0 of the Advanced Light Source, Lawrence Berkeley National Laboratory. In the XAS experiments, a Ge 2p core electron is excited into the empty states of the conduction band. If the nanocrystal conduction band minimum is blueshifted due to quantum confinement, the x-ray absorption threshold will be also shifted to higher energies. The initial starting point of a core electron makes the XAS technique highly element specific, making it an ideal tool to investigate deposited and surface-modified nanoparticles.

In Fig. 2 the XAS data of three nanocrystal depositions with varying thickness and a bulk

reference are shown. The average nanoparticle size is 1.6 nm. For the nanocrystal samples the actual data points are plotted and lines representing Savitzky-Golay smoothed data are added to guide the eye. The data from a very dilute sub-monolayer deposition (circles and dotted line) shows a large, 0.8 eV shift of the x-ray absorption edge of the germanium nanocrystals with respect to the bulk edge, indicating strong quantum confinement effects.⁶ The absorption edge of the very dilute sample and the bulk crystal are of comparable steepness and similar to earlier size-dependent XAS studies on bare particles no clear surface states can be distinguished.⁶ When the nanocrystal density on the substrate is increased and approaches a monolayer (diamonds and dashed line), the absorption edge is less shifted and exhibits a foot at the onset close to the bulk crystal value. The reduced edge shift indicates reduced quantum confinement effects in the nanocrystals. Finally, if more than one monolayer are deposited (triangles and dash-dotted line), the nanocrystal absorption edge lays in the vicinity of the bulk-crystal edge and no significant quantum shift can be determined.

The observed reduction of quantum confinement effects with increasing deposition coverage can be attributed to increasing particle – particle interaction. For the very dilute sub-monolayer deposition, the nanocrystals are well isolated and a sharp absorption onset and edge is measured. The edge shape and quantum shift of 0.8 eV agrees well with earlier investigations.⁶ In the intermediate regime approaching one monolayer of nanocrystals the particles are likely to be in contact with neighboring particles and form bonds. High-resolution transmission electron microscopy studies of deposited Ge nanocrystals⁵ have revealed both, highly ordered interfaces between two particles (twinning) and diffuse contact areas. In this context it should be noted that no coagulation, i.e., transfer of mass from one to another particle, could be observed in transmission electron and atomic force microscopy. Thus the nanocrystals retain their original size and shape upon contact. When the particles are juxtaposed to each other the excited electrons in the conduction band are not confined to one particle any longer and can move from one particle to another. These interacting nanoparticles can be described as larger aggregates with reduced quantum confinement. In an approximation, assuming that quantum confinement effects are proportional to the number of atoms in the aggregate and neglecting its shape, the effect of the particle interaction can be estimated. An aggregate of two particles with 1.6 nm and N atoms each, contains $2N$ atoms. The size of single particles scales with $N^{\frac{1}{3}}$ and therefore an equivalent particle with $2N$ atoms would exhibit a size of $1.6 \text{ nm} \cdot 2^{\frac{1}{3}} \approx 2.0 \text{ nm}$ with a corresponding conduction

band quantum shift of 0.4 eV.⁶ The upper part of the monolayer absorption edge in Fig. 2 exhibits a shift of 0.5 eV with respect to the bulk edge, suggesting a strong contribution to the overall edge from interacting double-particles. The foot at the absorption edge onset is shifted 0.2 eV and less with respect to the bulk crystals edge indicating contributions from larger particle aggregates. The absorption edge of the third sample, a deposition of multiple monolayers of nanocrystals, does not show any significant edge shift with respect to a bulk crystal, meaning that the quantum confinement effects are quenched. Here the particles form a three dimensional, widely interconnected network of interacting nanocrystals in which the quantum confining properties of the individual particles are effectively lost. It is interesting to note that the absorption edge of the thick film of particles is still significantly broadened compared to the dilute deposition of individual particles. Therefore it can be concluded that the dominating absorption edge broadening mechanism must be the distribution of quantum confinement effects and not e.g. surface states. Surface states would be reduced in strongly connected particle networks compared to individual nanoparticles.

This experiment shows that the nanocrystals need to be isolated, or more generally spoken that their particle – particle interaction needs to be suppressed, to keep their quantum confining properties. So far, the isolation has been achieved by spacial separation of the particles through diluting the sample heavily. An alternative approach is to isolate the individual particles by placing a barrier in between them. To do so, a procedure has been developed, in which the nanocrystal surface is terminated with methanol molecules. Methanol molecules are chosen because they have been previously shown to bond in a controlled manner on silicon surfaces.⁷ In detail, a sub-monolayer of germanium nanocrystals is deposited on the silicon substrate. Then the buffer gas is removed and in a second step methanol molecules are evaporated onto the particle surface. The evaporation parameters are a gas flow with a background pressure of 10^{-6} Torr in the vacuum chamber and an exposure time of 30 sec, corresponding to a passivant dose of 30 Langmuirs onto the sample. After methanol evaporation the chamber is pumped back down to 10^{-9} Torr and the procedure is repeated. The attachment process is characterized with core-level photoelectron spectroscopy. In Fig. 3 the Ge 3d core level spectra of an as-deposited (dotted line) and a passivated (solid line) nanocrystals film are shown. In order to obtain sufficient signal intensity from the deposited nanoclusters over the background and for comparison with earlier studies,⁸ particles with an average size of 4-5 nm are chosen for this investigation. The Ge 3d spectral shape of the as-

deposited and passivated nanocrystals are rather similar but for the passivated nanoparticles the surface states reported in previous studies⁸ cannot be fitted any longer and they exhibit additional spectral intensity in the sub-oxide regime at higher binding energies (shaded area in Fig. 3), indicating single-bonded surface attachments.⁹ Previous studies on the bonding of methanol to Si surfaces conclude that the attachment process works via a break-up of the OH-group and subsequent formation of both, Si–O–R and Si–H bonds.⁷ It is believed that a similar process is involved in the termination of the germanium nanocrystals. The efficiency of the passivation process can be roughly estimated. Gas phase aggregated Ge nanocrystals exhibit a reconstructed surface around a crystalline core.¹⁰ An ideal 4 nm Ge nanocrystal with reconstructed step edges and surface contains 1481 atoms and it exhibits 348 dangling bonds on the particle surface. Assuming that every dangling bond accepts one methanol molecule, 25% of the spectral intensity should be related to the particle – passivant interface. The shaded area in Fig. 3 exhibits roughly 12% of the overall peak area. Thus it can be concluded that the passivation routine is fairly efficient and saturates at least half of the surface atoms. In the likely case of a more aggressively reconstructed particle surface¹⁰ the number of dangling bonds is expected to be lower and thus the fraction of passivated surface atoms would be higher.

In Fig. 4 the x-ray absorption data for two passivated nanocrystal (average size 1.6 nm, similar to Fig. 2) depositions with greatly varying thickness are shown. Each spectrum represents one of the extreme conditions of Fig. 2. The circles in Fig. 4 are the data points from a very diluted sub-monolayer sample and the triangles are from a very thick multi-layer deposition. In strong contrast to the as-deposited nanocrystals (Fig. 2), both x-ray absorption edges of the passivated nanocrystal samples (Fig. 4) exhibit a similar threshold energy and there is no significant difference in their overall absorption edge shape. The additional feature in the passivated nanocrystal samples at 1221.5 eV can be attributed to the Ge – methanol bonds. In comparison, the very dilute as-deposited sample (Fig. 2) and the passivated nanocrystals (Fig. 4) exhibit a similar blueshift of 0.8 ± 0.1 eV at the inflection point of the absorption edge and the passivated nanocrystal spectra appear to be slightly broadened. The XAS results of the surface-terminated nanocrystal depositions can be understood in terms of suppressed particle – particle interaction. The attached methanol molecules introduce a barrier between the nanocrystals, effectively isolating them from each other. Hence, the excited electron in the conduction band remains confined to one particle

and the original properties of the nanocrystal remain intact, independent of the amount of material deposited. The observed similarities between the very dilute, as-deposited and the passivated nanocrystal films show that they both represent a similar system of individual, isolated particles. The tunability of the bandgap of passivated nanoparticles can be inferred from these results.

In conclusion, controlling the particle – particle interaction is of great importance for the resulting electronic structure of nanocrystal assemblies. Upon contact, as-deposited (bare) nanocrystals lose their quantum confining properties due to strong interaction between them. However, if the nanocrystals are isolated by means of surface termination, the particle – particle interaction can be suppressed and the nanocrystals retain their original properties independent of the film thickness. Through the combination of gas-phase based cluster synthesis and chemistry we are able to introduce a class of cluster-assembled materials with designed electronic properties through controlled particle – particle interaction. The present results are an important step towards nanocrystal materials synthesis, which will take advantage not only of the size-dependent but also of the interaction properties of its building blocks.

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FIG. 1: Nanocrystal deposition morphologies. Atomic force micrographs from a dilute, sub-monolayer (left) and a multi-layer (right) nanocrystal deposition on a silicon substrate. For better visualization larger particles with an average size of 5 nm are chosen.

FIG. 2: Quantum confinement in dependence of nanocrystal film thickness. Very diluted sub-monolayer depositions (circles) exhibit a strong blue-shift in their absorption edge due to quantum confinement. The edge shift diminishes with increasing coverage (diamonds) and is extinct for multilayer depositions (triangles).

FIG. 3: Surface termination characterization. Ge 3d photoelectron spectra of as-deposited (dotted line) and methanol terminated (solid line) nanocrystals. For the passivated nanocrystals additional spectral intensity (shaded area) in the sub-oxide regime can be distinguished, indicating covalent attachment of the methanol molecules to the nanocrystal surface.

FIG. 4: Quantum confinement in dependence of nanocrystal film thickness for passivated particles. In contrast to the as-deposited nanocrystals (Fig. 2) the nanocrystal absorption edges do not depend on the coverage. Both, dilute sub-monolayer (open circles) and multilayer (open triangles) deposition nanocrystals sample exhibit a strong blue-shift with respect to the bulk crystal.

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Fig. 1, Bostedt et al., Appl. Phys. Lett.

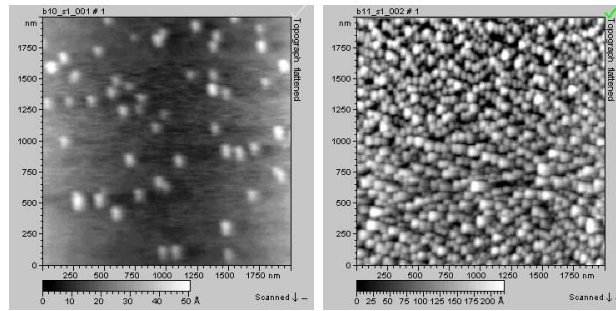


Fig. 2, Bostedt et al., Appl. Phys. Lett.

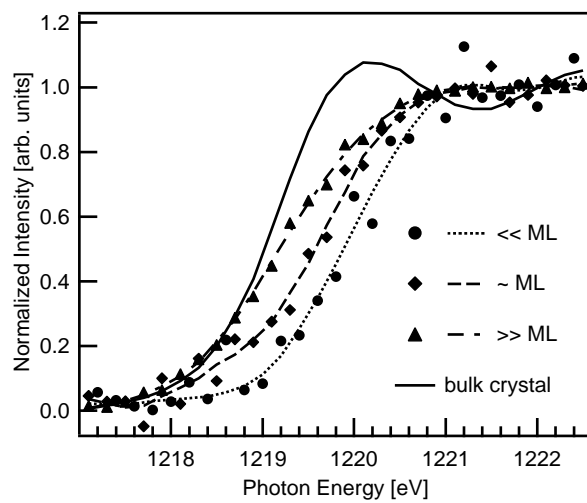


Fig. 3, Bostedt et al., Appl. Phys. Lett.

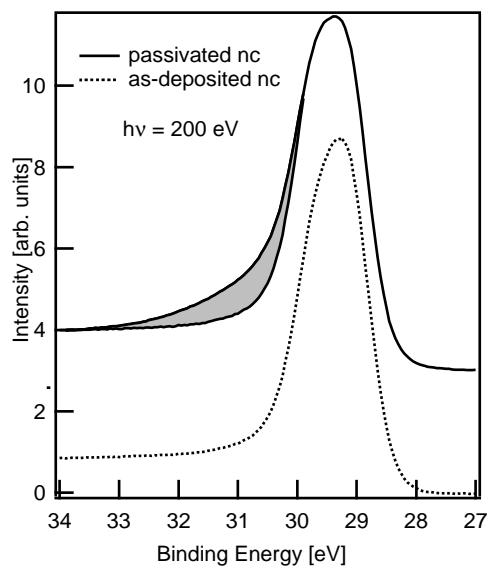


Fig. 4, Bostedt et al., Appl. Phys. Lett.

